

MEASUREMENT OF REACTION RATES IN NATURAL FLUID-ROCK SYSTEMS USING SR AND U ISOTOPES

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RESEARCH OBJECTIVES

A major need of the Department of Energy, and indeed a major objective of geochemistry, is to be able to predict the transport of chemical constituents in fluids in the earth. This applies to environmental remediation, geothermal and fossil energy resources, climate change science and nuclear waste isolation. One of the weak points in models for reactive chemical transport is the estimation of fluid-solid reaction rates, particularly for dissolution and precipitation reactions. Fluid-solid reaction rates are also important for predicting corrosion and weathering rates. Formulations can be made using kinetic theory, but it is a seemingly ubiquitous occurrence that other factors, some presumably involving mineral surfaces and others involving transport limitations on various scales, alter the predicted reaction rate by up to several orders of magnitude.

One means of addressing this issue is through the microscopic study of mineral surfaces, and substantial effort is now being made to do this using synchrotron radiation. A complementary and necessary approach, which we have taken, is to use isotopic tracers (primarily Sr, but also U and Nd) to determine fluid-solid exchange rates in various natural situations. The isotopic methods characterize the reaction rates in the system at the scale of the "reaction length." The reaction length depends on the ratio of the transport by diffusion and advection to the reaction rate, and can be anywhere from a few centimeters to hundreds of meters depending on the element used and the natural environment. The ultimate objective will be to understand the microscopic (as well as pore scale and mesoscale) characteristics of natural systems that contribute to establishing the "field scale" reaction rates. An intermediate goal is to establish empirically the natural range of fluid-solid reaction rates; if the range is limited and there are systematic variations, then a useful engineering-style tool is established.

APPROACH

To determine reaction rates, the Sr and U isotopic composition of fluids and rocks are measured in saturated zone groundwater, vadose zone groundwater, geothermal systems, deep sea pore fluids and in metamorphic rocks. The groundwater and geothermal systems are advective, the fluid velocities are meters to hundreds of meters per year (less in the vadose zone), and the reaction lengths for Sr are in the range of kilometers to hundreds of kilometers. In deep sea pore fluids and metamorphic systems, the transport in the fluid phase is mainly by diffusion; the reaction lengths vary from tens of centimeters to tens of meters. To determine the rates, the groundwater flow velocity (or fluid phase diffusivity) must be constrained. Uncertainties in these values are typically less than a factor of ± 3 .

RESULTS

Deduced fluid-solid exchange rates correspond to mineral dissolution time constants (grams dissolved/gram/yr) in the range 3×10^{-9} yr⁻¹ for the

slowest low temperature systems, to about 10^{-6} yr⁻¹ for the fastest high temperature systems (at ca. 600°C). The determined rates are not highly variable, show a significant but relatively weak temperature dependence, and are 2 to 8 orders of magnitude smaller than typical laboratory rates measured far from equilibrium. In some cases, empirically inferred rates combined with isotopic measurements can serve to constrain groundwater flow velocities; this is particularly useful for cases where the velocities are very small, such as the vadose zone at Yucca Mountain, Nevada. The differing reaction lengths for different elements (eg., Sr and O; or Sr and Nd) in the same system can also be exploited to extract information on the mesoscale hydrology (eg., fracture spacing) of some fluid-rock systems. Use of multiple isotope systems can help to identify the rates of specific reactions in complex natural systems.

SIGNIFICANCE OF FINDINGS

The results of these studies indicate that fluid-rock reaction rates can be deduced by measurements of the natural system at the scale of interest. The uncertainties in the deduced rates are far smaller than the uncertainties from application of kinetic theory, and can constitute a reasonably solid basis for predicting reactive chemical transport. The observation that reaction rates typically fall in a limited range is also useful.

RELATED PUBLICATIONS

Johnson, T.M., and D.J. DePaolo, Rapid exchange effects on isotope ratios in groundwater systems, 2. Flow investigation using Sr isotope ratios, *Water Resources Res.*, 33, 197-205, 1997.

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